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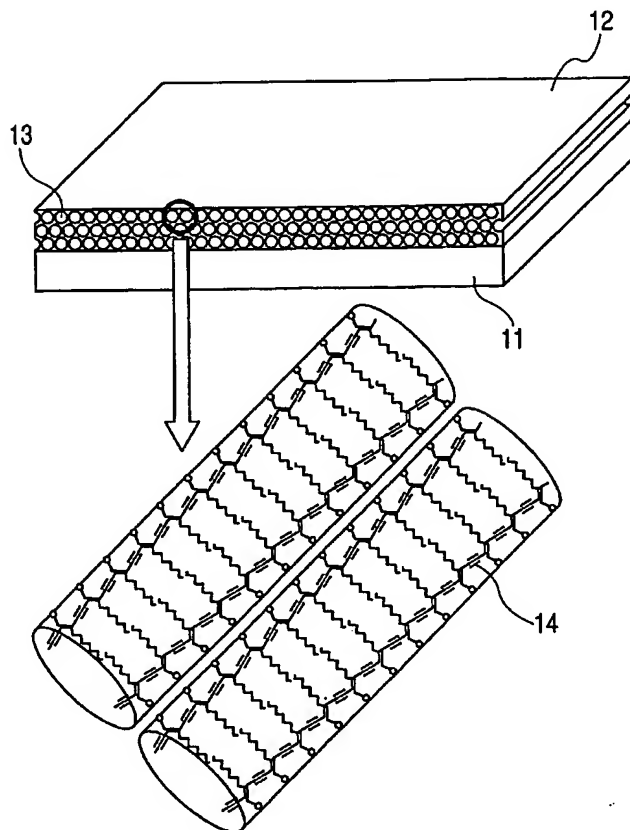
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(54) Title: **STRUCTURED MATERIAL AND PRODUCING METHOD THEREOF**



(57) Abstract: The invention provides a structured material characterized in having, on a substrate (11), a layer (12) having tubular (13) pores positioned uniaxially parallel to the interface of the substrate and the layer and supporting a conductive polymer material (14,21) having a function of a surfactant (22) therein. The invention also provides a method for producing the above structure material characterized by the steps of providing a substrate having the anisotropy on a surface, applying a solution containing a surfactant having a functional group for polymerization in the molecular structure, a solvent therefor, and a solute different from the surfactant to the substrate, and a step of standing for a predetermined time for causing the surfactant to assemble in a predetermined direction based on the anisotropy of the substrate.

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DESCRIPTION

STRUCTURED MATERIAL AND PRODUCING METHOD THEREOF

5 This application claims priority from Japanese Patent Application No. 2003-278340 filed on July 23, 2003, which is hereby incorporated by reference herein.

10 TECHNICAL FIELD

 The present invention relates to a structured material including a polymer compound, and more particularly to a technology for orienting chains of a polymer utilizing a pore-orienting technology.

15

BACKGROUND ART

 Conductive polymers are being actively investigated because of their potential in production of inexpensive organic transistors. Conductive
20 polymers have a structure in which a conjugated chain extends as a main chain, and show a high conductivity in such a direction. However, such conductive polymers are utilized in a bulk state because of absence of effective technology for orienting main
25 chains of the conductive polymer, and sufficient electroconductivity is currently not obtained because the conduction between the polymer chains is achieved

by the hopping conduction. For orienting the polymer chains, investigations are being proceeded, for example, utilizing a Langmuir-Blodgett film.

A structured material prepared by using
5 molecular assemblies of surfactants as a template has a structure in which molecular assemblies of the surfactant are regularly arranged by self-organization in a matrix of an inorganic compound. Particularly a structured material having pores of an
10 average diameter of 2 to 50 nm is called a mesoporous structure, which is called a mesostructured material in the present description. A structured material of which pores are filled with a material is also called a mesostructured material. Initially, the inorganic
15 compound was limited to silica, but such a structure can now be prepared with various materials such as oxides, metals or sulfides, a structure of which pore walls are constituted of an inorganic-organic nanocomposite material is now also available. Also
20 the originally found material was in a powder state, but now various forms such as a film, a fiber, a sphere etc., are available.

The mesostructured material, having a possibility of introducing another material into
25 regular nanospaces thereby controlling structure or orientation of such material, is expected for applications in electronic materials and optical

materials in addition to conventional applications of porous materials such as an adsorption/separation material or a catalyst, and investigations are being made in wide fields. For introducing a material into pores of a mesostructure material, there are principally two methods. One is to eliminate the surfactant assemblies constituting pores and introduce a guest material into thus formed hollow pores. This method is generally employed for mesoporous silica, but cannot be applied to a material of which mesostructure is destructured by the elimination of the surfactant assemblies. This method has a difficulty in introduction of a bulky guest species such as a polymer material when the structure is a film or the like. The other method is to make the guest species to be inserted coexist the preparation of a mesostructured material, whereby the guest species is held in the pores at the preparation. This method has an advantage that it is applicable to a wide range of mesostructure materials since the surfactant need not be eliminated, but there is a considerable limitation to the guest species that can be introduced by this method.

There is recently reported a technology of forming a functional material in pores by a method other than these two methods. This method is based on providing the surfactant itself with a

functionality and preparing a mesostructured material having a functional material in the pores without eliminating the surfactant. This method is applied to a film, or a fiber as described in *Angewandte Chemie*, International Edition, 40, pp3803-3806, in which a mesostructured material is prepared by using surfactants having a polymerizable functional group in the molecular structure and then polymerization is achieved by heat etc., thereby preparing conductive polymer chains in the pore.

However, the aforementioned method of preparing a mesostructured material utilizing surfactants having a polymerizable functional group in the molecular structure is difficult to practice because of the following reasons.

In a film employed in prior technologies, tubular pores in the film plane have random directions so that the polymer chains have random directions macroscopically even if a polymer chain is formed along the pore direction. On the other hand, a fibered structure is small and difficult to handle, and also as described in *Advanced Materials*, 12, pp961-965, a pore formed a spiral in the fiber. Consequently, even if the polymer chain is oriented along the direction of the pore, the polymer chain assumes a spiral form in this method so that it is difficult to control the direction of the polymer

chain by the pores.

On the other hand, *Science*, 288, pp652-656 describes a partial orientation of a conductive polymer compound utilizing a mesostructured silica monolith of which pore direction is oriented by strong magnetic field. This method eliminates the surfactant by calcination after the preparation of a mesostructured silica and to introduce a conductive polymer compound into thus formed hollow nanospace, but the obtained mesostructured silica, having numberless fine cracks, is difficult to apply to an optical material or an electronic material, and an alignment control of conductive polymer main chains over the entire structure is not achieved as the polymers present in such cracks are random.

The present invention is to achieve an orientation control of polymer chains in a macroscopic scale, utilizing a meso-structured film in which tubular pores are oriented in one direction.

DISCLOSURE OF THE INVENTION

The present invention provides a structured material formed by a layer having tubular pores on a substrate, in which the tubular pores are positioned parallel to the interface of the substrate and the layer, and a conductive polymer is held in the tubular pores.

The present invention also provides a production method for a structured material, which comprises the steps of: applying a solution . containing surfactants that has a polymerizable functional group in the molecular structure, a solvent, and a solute different from the surfactants, onto a substrate having anisotropy, and the step of leaving the product of the above step standing for a predetermined time for causing the surfactant to assemble in a direction on the basis of the anisotropy of the substrate.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a schematic view of a meso-structured film prepared in the present invention including orienting conjugated polymer chains in pores.

Fig. 2 is a schematic view of a meso-structured film before polymerization.

Fig. 3 is a schematic view showing an apparatus for preparing a Langmuir-Blodgett film to be employed in the present invention.

Fig. 4 is a schematic view showing a reaction vessel for preparing, in the present invention, a meso-structured film having orienting tubular pores by heterogeneous nucleation and growth.

Figs. 5A, 5B, 5C, 5D, and 5E show chemical structures of surfactants advantageously employed in

the present invention.

Fig. 6 is an another schematic view of a meso-structured film prepared in the present invention including orienting conjugated polymer chains in pores.

Fig. 7 is a schematic view showing a dip coating apparatus for preparing a film to be employed in the present invention.

10 BEST MODE FOR CARRYING OUT THE INVENTION

An oriented meso-structured film including a conjugated polymer in the present invention has a structure schematically shown in Fig. 1, for example. On a substrate 11 having a structural anisotropy at the surface, a meso-structured film 12 having tubular pores of a honeycomb structure is formed. In the meso-structured film, tubular mesopores 13 are oriented in one direction. In the pore, as illustrated, a conjugated polymer is formed by polymerization of surfactants. The present inventors estimate that a single tubular pore contains plural conjugated polymer chains 14 (Fig. 1) or 21 (Fig. 6). The conjugated polymer chain 14 indicates a polydiacetylene derivative, while the chain 21 indicates a polypyrrole derivative.

The oriented meso-structured film including the conjugated polymer in the present invention is formed

by causing polymerization reaction of the surfactant molecules in the pores formed by assemblies of surfactants 22 having a polymerizable functional group as a template. The film before polymerization is also an embodiment of the present invention. The surfactant assemblies exist in a tubular formation in a composite material, and its cross section is schematically illustrated by 21 in Fig. 2.

In the following, there will be given detailed descriptions on methods of producing an oriented meso-structured film of the present invention, including the conjugated polymer compound, and a detailed configuration thereof.

In configurations shown in Figs. 1 and 2, the numeral 11 denotes a substrate having a structural anisotropy on the surface. The substrate having the surface anisotropy employable in the present invention generally belongs to one of the following two categories. One is a crystalline substrate having a strong anisotropy in an atomic arrangement on the surface, and the other is an ordinary substrate such as glass on which surface a material having a structural anisotropy is provided.

The method of utilizing a crystalline substrate having a strong anisotropy in the atomic arrangement on the surface requires the use of a relatively expensive monocrystalline substrate, but has an

advantage that a mesostructured material having oriented tubular pores can be directly formed on the substrate. In such a case, when a conductive monocrystalline substrate is used, a satisfactory electric contact between the substrate and the conductive polymer in the pore is expected. A preferable crystalline substrate with a strong anisotropy in the atomic arrangement is a substrate of which surface atomic arrangement shows two-fold symmetry. On the surface of such a crystalline substrate, the direction of specified arrangement of atoms is uniquely determined, thereby realizing an ability of orienting the surfactant assemblies. There is preferably employed a single crystal substrate having a diamond-like crystal structure or the (110) plane of a single crystal substrate of a sphalerite-like crystal structure, particularly the (110) plane of silicon.

A method of forming a material having a structural anisotropy on a surface of an ordinary substrate, though involving an extremely thin layer between the substrate and the mesostructured material, has an advantage of achieving a highly uniaxial orienting property with an inexpensive material. As a material having a structural anisotropy on the surface of the substrate, there is advantageously employed a Langmuir-Blodgett film of a polymer or a

polymer film subjected to a rubbing process.

First, a method for preparing a substrate will be explained.

When a crystalline substrate having a surface
5 atomic arrangement with twofold symmetry is used for
preparation of a mesostructured material, the
substrate is sufficiently washed to expose a clean
crystal surface. Then, for example, in a case of a
'silicon substrate, a spontaneous oxide film on the
10 surface is eliminated. This can be achieved by a
simple process, for example, by treating the surface
with diluted hydrofluoric acid for several minutes.
A substrate with a crystal surface exposed by such
- treatment can be directly employed in the preparation
15 of a mesostructured film to be explained later.

Then a case where a material having a
structural anisotropy is formed on a surface of an
ordinary substrate will be explained.

First, there will be explained a method of
20 forming a Langmuir-Blodgett film (LB film) of a
polymer compound. The LB film is formed by
transferring a monomolecular film, developed on a
water surface, onto the substrate, and can be formed
as a film of a desired number of layers by repeating
25 this film formation. The term LB film used in the
present invention includes laminated monomolecular
films of an LB film derivative, formed by a heat

treatment or the like to an LB film formed on the substrate to modify the chemical structure while maintaining the laminated structure.

The LB film can be prepared by an ordinary method. An ordinary LB film forming apparatus is schematically shown in Fig. 3. In Fig. 3, there are shown a tank 31 filled with pure water 32, and a fixed barrier 33 with a surface pressure sensor (not shown). A monomolecular film 36 on the water surface is formed by dropping a liquid, in which a desired substance or a precursor of a desired substance is dissolved, onto the water surface in an area between the barrier 33 and a movable barrier 34. A surface pressure is applied to the film by a movement of the movable barrier 34. The movable barrier is position-controlled by the surface pressure sensor in such a manner that a constant surface pressure is applied during the film formation on the substrate. The pure water is maintained in a clean state by a water supply apparatus and a water discharge apparatus (not shown). The water tank 32 is provided with a hole, at which position a substrate 35 is held to be moved vertically at a constant speed by a translation movement device (not shown). The film on the water surface is taken up onto the substrate when it is immersed into water or extracted therefrom.

The LB film employed in the present invention

is formed on the substrate as a monomolecular layer at a time, by applying a surface pressure to a monomolecular layer formed on the water surface in the aforementioned apparatus and immersing and
5 extracting the substrate into and from the water. The form and properties of the film are controlled by the surface pressure, the moving speed of the substrate in immersion/extraction, and the layer number. The optimum surface pressure at the film
10 formation is determined according to a surface area-surface pressure curve, but is generally within a range from several to several tens of mN/m. Also the moving speed of the substrate is generally within a
- range from several to several hundred mm/min. The
15 number of layers is suitably determined within a range from several layers to several hundred layers. The LB film formation is generally prepared by the aforementioned method, but it is not limited to such method in the present invention and there can also be
20 employed, for example, a method utilizing a flow of water constituting a sub-phase.

A material constituting the LB film is not particularly limited as long as it can withstand a process for forming a meso-structured film to be
25 explained later and is capable of controlling uniaxial orientation of pores in the mesostructure, and, for example, polyimide can be advantageously

employed.

In the following, there will be explained a method of utilizing a substrate bearing a polymer film subjected to a rubbing process. The rubbing
5 process is a method of coating a polymer on the substrate, for example, by spin coating, and rubbing such coating with a cloth or the like. The rubbing cloth is wound on a roller, and the rubbing is prepared by contacting the rotating roller with the
10 surface of the substrate and moving a stage supporting the substrate in a direction with respect to the roller.

The rubbing cloth is optimally selected according to the polymer material to be used, but can
15 be an ordinary material such as nylon or rayon. The rubbing intensity is optimized by parameters such as the revolution of the roller, pressure of the roller to the substrate, and the moving speed of the stage supporting the substrate.

20 In the following a method for forming a meso-structured film on the substrate will be explained. The method for forming a meso-structured film on the substrate is classified largely into two categories; one being based on heterogeneous nucleation and
25 growth from a solution to a surface of a substrate, while the other being based on a sol-gel method.

First, a method based on heterogeneous

nucleation and growth occurring at the solid-liquid interface will be explained. This method is principally used for preparing a meso-structured silica film by a process similar to crystal growth.

5 In this method, an aforementioned substrate is maintained in a precursor solution containing a raw material for a desired pore wall constituting material in an aqueous solution of surfactants, whereby a meso-structured film is formed on the
10 substrate.

A reaction vessel to be used for the formation of the meso-structured film, for example, has a structure as shown in Fig. 4. The material constituting the reaction vessel 41 is not
15 particularly limited as long as it does not affect the reaction, and can be, for example, polypropylene or Teflon (registered trade name). The reaction vessel may be placed in a closed container of a highly rigid material such as stainless steel, in
20 order that it is not destructed even in case a pressure is applied during the reaction. In the reaction vessel, a substrate holder 43 is provided as shown in Fig. 4, for supporting a substrate 45. During the reaction, the formation of the
25 mesostructured material takes place not only on the substrate but also in the solution, so that a precipitate in the solution is deposited onto the

substrate. In order to prevent such situation, the substrate is held facedown, i.e., with the film forming surface downward, in the solution during the reaction.

- 5 The reaction solution is formed by adding an acid etc., to an aqueous solution of surfactants for regulating to pH value suitable for formation of a desired pore wall, and adding a raw material substance such as an alkoxide for a desired material.
- 10 A preferable alkoxide is one that generates water-soluble alcohol by hydrolysis.

 The surfactant to be employed is provided, in the molecular structure, with a functional group capable of forming a conjugated polymer by

15 polymerization, and is preferably a cationic surfactant having ammonium as a hydrophilic group as indicated by Fig. 5B, 5D or 5E, or a nonionic surfactant having polyethylene oxide as a hydrophilic group as indicated by Fig. 5A or 5C.

- 20 However, the usable surfactant is not limited to these. Also, the length of a hydrophobic group and the size of a hydrophilic group in the surfactant molecule are determined according to the pore size of a desired mesostructure. The position of the
- 25 polymerizable functional group in the molecular structure is so determined as to do an optimum polymerization behavior.

The functional group capable of forming a polymer compound by polymerization is preferably a diacetylene group, a pyrrole group, a thiophene group etc., and a surfactant containing such a group in the structure can provide polydiacetylene, polypyrrole, polythiophene etc., as will be explained later. However, the functional group capable of forming a polymer compound applicable in the present invention and the formed polymer compound are not limited to the foregoing examples, and any conjugated polymer compound that can be formed by polymerization in the pore may be employed.

In the present invention, the aforementioned substrate having the structural anisotropy on a surface is placed in the above-explained precursor solution and is maintained for 1 to 10 days at temperature optimized for the compound constituting the desired pore wall, whereby a meso-structured film having tubular pores in controlled direction is formed on the substrate. The film thickness can be controlled, for example, by the reaction time. In such a mesostructured material, the assemblies of surfactants having a polymerizable functional group in the molecular structure constitute a template for the tubular pore.

In the following a method based on sol-gel process will be explained. It is a simple method

applicable to the preparation of a meso-structured film of various materials, and is composed of coating a precursor solution, containing surfactants and a pore wall raw material, on a substrate, evaporation of solvents, hydrolysis and condensation.

The precursor solution employed in this method is formed by adding a raw material for the pore wall constituting material to solution of surfactants. For the solvent, an alcohol such as ethanol or isopropanol is advantageously employed, but this is not restrictive and, for example, a mixture of alcohol and water or water may be used depending on the desired pore wall material.

The raw material for the pore wall is not particularly limited as long as it can form the desired material by hydrolysis, and can advantageously be a metal halide or an alkoxide, particularly preferably tin chloride, tin alkoxide, titanium chloride, titanium alkoxide, silicon chloride or silicon alkoxide.

The surfactant to be employed includes in the molecular structure, as in the case of the method based on heterogeneous nucleation and growth, a functional group capable of polymerization to form a conjugated polymer. In this method, there is preferably employed surfactants including polyethylene oxide as a hydrophilic group. Therefore,

among the structures shown in Figs. 5A to 5E, those indicated by Fig. 5A and 5C are usable. However, the usable surfactant is not limited to such structures. Also in the surfactant molecule to be used, a length
5 of a hydrophobic group and a size of a hydrophilic group are determined according to pore size of a desired mesostructured material. The position of the polymerizable functional group in the molecular structure is so determined as to do an optimum
10 polymerization behavior.

The precursor solution of the above-described composition is applied on the aforementioned substrate having the anisotropy, or placed on an arbitrary position thereon. The coating can be
15 achieved by various methods such as dip coating, spin coating or mist coating. Other coating methods capable of uniform coating are also applicable. An apparatus for spin coating or dip coating can be an ordinary one without particular restriction, but
20 means for controlling the temperature of the solution, and means for controlling temperature and humidity of the atmosphere for coating may be provided in certain cases.

As an example, a method for producing a
25 mesostructured thin film utilizing dip coating will be explained. An example of the apparatus used for dip coating is illustrated in Fig. 7, in which a

container 71, a substrate 72, and a precursor solution 73 are shown.

A substrate to be subjected to formation of a meso-structured film is fixed by a substrate holder
5 74 to a rod 75, and is vertically moved by a z-stage 76. The direction of anisotropy of the substrate may be selected in an arbitrary direction with respect to the direction of dip coating.

At the film formation, the precursor solution
10 73 is heated at desired temperature, utilizing a heater 78 and a thermocouple 77 if necessary. In order to improve the control on the solution temperature, the entire container may be placed in a heat insulating container (not shown). The thickness
15 of the film can be controlled by varying coating conditions.

Also for positioning the precursor solution in an arbitrary position on the substrate, various methods can be employed, such as a micro-contact
20 printing method, an ink jet method or a pen lithography method. These methods allow to pattern the meso-structured film in a desired position on the substrate.

The substrate coated with the solution is dried
25 by evaporating the solvent in an atmosphere of from room temperature to about 60°C. Then, if necessary, it is exposed to water vapor by holding the substrate

in high temperature atmosphere. The inventors estimate that, in these drying and vapor exposure steps, tubular assemblies of the surfactants are subjected to a structural anisotropy of the substrate
5 whereby the pores are uniaxial orientation.

Through the method explained in the foregoing, a meso-structured film is obtained in which assemblies of the surfactants, having a polymerizable group in the molecular structure, are included in
10 tubular pores. This film is defined as a precursor film for an oriented meso-structured film including a conjugated polymer, explained in the following.

The precursor meso-structured film prepared as explained above is subjected to thermal or light
15 stimulation to polymerize the surfactant molecules present in each pore, thereby forming a polymer compound in the pore. A surfactant having a diacetylene group in the molecular structure allows to obtain a conjugated polymer polydiacetylene in the
20 pore.

Polydiacetylene can be confirmed by infrared absorption spectroscopy and fluorescence spectroscopy, and the orientation of the polymer main chain in the pore can be confirmed by measuring polarized light in
25 absorption spectroscopy and light emission spectroscopy.

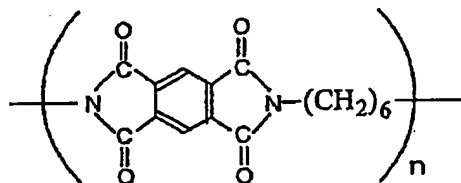
In the following, the present invention will be

further clarified by examples.

Example 1

In this example, a meso-structured silica film including uniaxially oriented tubular pores on a substrate was formed by employing a substrate subjected to a rubbing process, a cationic surfactant containing a diacetylene group and a heterogeneous nucleation/growth. Thermal polymerization of the surfactants was carried out in the oriented pores thereby forming a conjugated polymer compound having an oriented polymer chain.

A silica glass substrate was rinsed with acetone, isopropyl alcohol and pure water and subjected to surface cleaning in an ozone generating apparatus, spin-coated with an NMP solution of polyamic acid and baked for 1 hour at 200°C to convert to polyimide A coating of the following structure:



It was then subjected to a rubbing process under conditions shown in Table 1 to obtain a substrate.

[Table 1]

Cloth material	Nylon
Roller diameter (mm)	24
Press-in amount (mm)	0.4
Revolution (rpm)	1,000
Stage speed (mm/min)	600
Number of repetition	2

On this substrate, a meso-structured silica film was formed utilizing surfactants that have a polymerizable group in the molecular structure.

The cationic surfactant A employed in the present invention has the following molecular structure:



0.36 g of the surfactant A were dissolved in 12.8 ml of pure water, and 6.8 ml of concentrated hydrochloric acid (36%) were added. Then 0.28 ml of tetraethoxysilane were added and the mixture was stirred for 3 minutes.

The substrate with the rubbing-treated polyimide was held in this reactant solution with the polyimide surface downwards, then the vessel containing the reaction solution was sealed at 80°C for 3 days for the formation of a mesostructured silica film. In order to achieve the satisfactory uniaxial alignment of the mesopores in the

mesostructured silica film, the surface was covered with another silica glass plate using a spacer during the reaction. The reaction vessel employed was as schematically shown in Fig. 4.

5 The substrate in the reactant solution for the predetermined time was taken out from the vessel, and rinsed sufficiently with pure water and was dried at the room temperature in an ambient atmosphere. On the substrate, there was formed a continuous meso-
10 structured silica film, which showed, in observations by an optical microscope, uniaxially oriented textures in a direction perpendicular to the rubbing direction, thereby suggesting an orientation of the pore.

15 X-ray diffraction analysis of this film confirmed a strong diffraction peak assigned to the (100) plane of hexagonal porous structures corresponding to a plane interval of 3.56 nm, thereby confirming that the film had a pore structure in
20 which tubular pores are hexagonally packed.

 For quantitative evaluation of uniaxial orientation of the tubular pores in this meso-structured silica film, this film was analyzed by in-plane X-ray diffraction. This method measures the
25 in-plane rotational dependence of the X-ray diffraction intensity resulting from the (110) plane perpendicular to the substrate, as described in

Chemistry of Material, vol.12, p.49, and can determine the orienting direction of the pores and its distribution. The in-plane rotation angle dependence of the diffraction intensity on the (110) plane, measured in the present example, indicated that the pores in the meso-structured silica film prepared in the present example were oriented perpendicular to the rubbing direction of the polyimide film, and the distribution of the orientation direction was about 12° from the full width of the half maximum of the diffraction peak in the in-plane rocking curve.

Based on the foregoing, it is shown that a meso-structured silica film having tubular pores of an uniaxial orientation can be formed on a substrate with a rubbing-treated polyimide film, utilizing surfactants containing a polymerizable diacetylene group as a hydrophobic group.

Such a meso-structured film was heated for 3 hours at 170°C in a nitrogen gas atmosphere to polymerize the diacetylene group of the surfactants. Infrared absorption spectroscopy of the meso-structured film were taken by an ATR method before and after heating. As a result, a strong absorption band of an acetylene bond at $2,260\text{ cm}^{-1}$ observed before heating vanished after the heating, while other peaks did not show change. This result

confirmed that the polymerization took place without decomposition of the surfactant molecules. Also fluorescence, not observed in the film before heating, was observed in the film after heating, thus confirming formation of polydiacetylene in the pores. Investigation of the polarizing characteristics of the observed fluorescence indicated that the polarization direction of fluorescence is confirmed in perpendicular to the rubbing direction, namely along the direction of the oriented pores, thereby confirming orientation control of the polymer chains in the pores and orientation control of the conjugated polymer chains in a macroscopic scale.

Example 2

In this example, an uniaxially oriented mesostructured film was prepared by employing the same surfactant A as in Example 1 and the silicon (110) single crystal substrate, to form polydiacetylene in the oriented pores.

The same reactant solution and the vessel were used for preparing the mesostructured silica as in Example 1.

The substrate was the Si (110) of p-type polished on one side and having a specific resistance of 100 Ωcm . It was cut into a size of 2 × 2 cm, then treated with a 1% solution of hydrofluoric acid for eliminating the spontaneous oxide film on the surface

before use. The elimination of the oxide film can be confirmed by a fact that the surface of the silicon wafer becomes hydrophobic after the film elimination. After this process, the substrate was sufficiently
5 rinsed with pure water, held by a substrate holder with the polished surface downwards, placed in reactant solution in a Teflon (registered trade name) vessel. The vessel was sealed for 3 days at 80°C for the formation of a mesostructured silica film.

10 The substrate in the reactant solution for the predetermined time was taken out from the vessel, and rinsed sufficiently with pure water and was dried at the room temperature. A continuous meso-structured
- silica film was formed on the substrate. Observation
15 by an optical microscope showed uniaxially oriented textures, suggesting an orientation of the pore.

X-ray diffraction analysis of this film confirmed, as in Example 1, a strong diffraction peak assigned to the (100) plane of hexagonal porous
20 structures corresponding to a plane interval of 3.56 nm, thereby confirming that the film had a pore structure in which tubular pores are hexagonally packed.

The uniaxial orientation of the tubular pores
25 in this meso-structured silica film was analyzed by the in-plane X-ray diffraction as in Example 1. As a result, the distribution of orientation direction in

the film prepared in the present example was about 29° from the full width of the half maximum of the diffraction peak in the in-plane rocking curve.

Based on the foregoing, it was shown that a
5 meso-structured silica film having tubular pores of an uniaxial orientation was formed on the silicon (110) plane, utilizing surfactants containing a polymerizable diacetylene group as a hydrophobic group. The meso-structured film of the present
10 example have the distribution of orientation of the pores wider than that in the film prepared in Example 1, but have advantages that a rubbing-treated step is unnecessary and the film can be prepared directly on the conductive substrate.

15 This meso-structured film was irradiated for 4 hours with an ultraviolet light of 254 nm by using a high pressure mercury lamp. Infrared absorption spectroscopy of the meso-structured film were taken by an ATR method before and after irradiation. As a
20 result, a strong absorption band of an acetylene bond at 2,260 cm⁻¹ observed before irradiation decreased in intensity after the irradiation, while other peaks did not show change. This result confirmed that the polymerization took place without decomposition of
25 the surfactant molecules. Also fluorescence, not observed in the film before irradiation, was observed in the film after the irradiation, thus confirming

formation of polydiacetylene in the pores.

Investigation of the polarizing characteristics of the observed fluorescence indicated that the polarization direction of fluorescence is confirmed
5 along the $\langle 001 \rangle$ direction of the Si substrate, namely along the direction of the oriented pores, thereby confirming orientation control of the polymer chain in the pores and orientation control of the conjugated polymer chains in a macroscopic scale.

10 The method utilizing photopolymerization has, as in the present example, a possibility that the polymerization is not complete as shown by the infrared absorption spectroscopy, but has an advantage that a portion of polymerization can be
15 patterned by light irradiation through a mask.

Example 3

In this example, an uniaxially oriented meso-structured film was prepared by employing the same surfactant A as in Examples 1 and 2, and a silica
20 glass substrate coating a Langmuir-Blodgett film, and polydiacetylene was prepared in the oriented pores. A Langmuir-Blodgett film was prepared with polyimide used in Example 1, and the same reactant solution and vessel were used as in Examples 1 and 2.

25 Polyamic acid A and N,N-dimethylhexadecylamine were mixed in 1:2 molar ratio to obtain an N,N-dimethylhexadecylamine salt of polyamic acid A. It

was dissolved in N,N-dimethylacetamide to obtain 0.5 mM solution, which was dropped onto the surface of water in an LB film forming apparatus, maintained at 20°C. A monomolecular film formed on the water surface was transferred onto the substrate with a dipping speed of 5.4 mm/min under a constant surface pressure of 30 mN/m.

The substrate was a silica glass substrate rinsed with acetone, isopropyl alcohol and pure water, then subjected to surface cleaning in an ozone generating apparatus, and a hydrophobic treatment.

Thirty layers of LB films of polyamic acid alkylamine salt were formed on the substrate, and were baked for 30 minutes at 300°C to convert to polyimide A. An imidization by dehydration ring-closing of polyamic acid and liberation of alkylamine were confirmed by infrared absorption spectroscopy. An orientation of the polymer chain in thus formed polyimide LB film was analyzed by dichroic properties of infrared absorption spectroscopy, and was confirmed to be parallel to an extracting direction of the substrate at the LB film formation.

The same surfactant A containing a diacetylene group in the molecular structure as in Examples 1 and 2 was employed to prepare a precursor solution of the same composition as in Examples 1 and 2. The substrate coating the aforementioned layered LB film

was supported in this solution with the film-coating surface downwards, then the vessel containing the reactant solution was sealed for 3 days at 80°C for the formation of a mesostructured silica film. In order to achieve the satisfactory uniaxial alignment of the pores in the meso-structured silica film, the surface was covered with another silica glass plate using a spacer during the reaction.

The substrate in the reactant solution for the predetermined time was taken out from the vessel, and rinsed sufficiently with pure water and was dried at the room temperature. On the substrate, there was formed a continuous meso-structured silica film, which showed, in observations by an optical microscope, an uniaxially oriented texture in a direction perpendicular to the extracting direction of the substrate, thereby suggesting an orientation of the pore.

X-ray diffraction analysis of this film confirmed a strong diffraction peak assigned to the (100) plane of hexagonal porous structure corresponding to a plane interval of 3.60 nm, thereby confirming that the film had a pore structure in which tubular pores are hexagonally packed.

For quantitative evaluation of uniaxial orientation of the tubular pores in this meso-structured silica film, this film was analyzed by in-

plane X-ray diffraction. As a result, it was indicated that the alignment of pores in the prepared film were oriented perpendicular to the extracting direction of the substrate and the distribution of the orientation direction was about 15° from the full width of the half maximum of the diffraction peak in the in-plane rocking curve.

Based on the foregoing, it was shown that a meso-structured silica film having tubular pores of an uniaxial orientation was formed on the substrate coating a polyimide LB film, utilizing surfactants containing a polymerizable diacetylene group as a hydrophobic group.

The above meso-structured film was heated for 3 hours at 170°C in a nitrogen gas atmosphere to polymerize the diacetylene group of the surfactant. Infrared absorption spectroscopy of the meso-structured film were taken by an ATR method before and after heating. As a result, a strong absorption band of an acetylene bond at 2,260 cm⁻¹ observed before heating vanished after the heating, while other peaks did not show change. This result confirmed that the polymerization took place without decomposition of the surfactant molecules. Also fluorescence, not observed in the film before heating, was observed in the film after the heating, thus confirming formation of polydiacetylene in the pores.

Investigation of the polarizing characteristics of the observed fluorescence indicated that the polarization direction of fluorescence is confirmed in perpendicular to the extracting direction of the substrate, namely along the orientation direction of the pores, thereby confirming orientation control of the polymer chain in the pores and orientation control of the conjugated polymer chains in a macroscopic scale.

10 Example 4

In this example, an uniaxially oriented meso-structured film in which tubular pores were oriented in a direction and of which pore wall is constituted of inorganic-organic nanocomposites was prepared by employing a substrate with the rubbing-treated polyimide film as in Example 1 and the same surfactant A as in Examples 1 to 3, and employing a precursor (silicon alkoxide A) represented by the following structural formula instead of the silicon alkoxide employed in Examples 1 to 3, and a conjugated polymer chain was polymerized in the pores.



0.36 g of the surfactant A were dissolved in 12.8 ml of pure water, and 3.8 ml of concentrated hydrochloric acid (36%) were added. Then 0.50 g of the aforementioned silicon alkoxide A were added and

the mixture was stirred for 3 minutes.

The substrate with rubbing-treated polyimide was supported in this reactant solution with the polyimide surface downwards, then the vessel
5 containing the reactant solution was sealed for 3 days at 70°C for the formation of a mesostructured silica film. In order to achieve the satisfactory uniaxial alignment of the pores in the meso-structured silica film, the surface was covered with
10 another silica glass plate using a spacer during the reaction.

The substrate in the reactant solution for the predetermined time was taken out from the vessel, and
- rinsed sufficiently with pure water and was dried at
15 the room temperature in an ambient atmosphere. On the substrate, there was formed a continuous meso-structured silica film, which showed, in observations by an optical microscope, an uniaxially oriented texture in a direction perpendicular to the
20 rubbing direction, thereby suggesting an orientation of the pore.

X-ray diffraction analysis of this film confirmed a strong diffraction peak assigned to the (100) plane of hexagonal porous structures
25 corresponding to a plane interval of 3.48 nm, thereby confirming that the film had a pore structure in which tubular pores are hexagonally packed.

For quantitative evaluation of uniaxial orientation of the tubular pores in this meso-structured silica film, this film was analyzed by in-plane X-ray diffraction. As a result, it was indicated that the pores in the meso-structured silica film prepared in the present example were oriented perpendicularly to the rubbing direction of polyimide, and the distribution of the orientation direction was about 14° from the full width of the half maximum of the diffraction peak in the in-plane rocking curve.

Based on the foregoing, it was shown that a meso-structured silica film having tubular pores of an uniaxial orientation of which pore wall was constituted of a silica-organic hybrid material, was formed on a substrate with the rubbing-treated polyimide film, utilizing surfactants containing a polymerizable diacetylene group as a hydrophobic group.

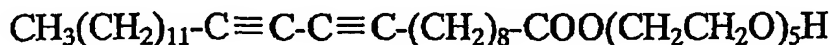
The above meso-structured film was heated for 3 hours at 170°C in a nitrogen gas atmosphere to polymerize the diacetylene group of the surfactant. Infrared absorption spectroscopy of the meso-structured film were taken by an ATR method before and after heating. As a result, a strong absorption band of an acetylene bond at $2,260\text{ cm}^{-1}$ observed before heating vanished after the heating, while

other peaks did not show change. This result confirmed that the polymerization took place without decomposition of the surfactant molecules and the organic component in the pore wall. Also
5 fluorescence, not observed in the film before heating, was observed in the film after the heating, thus confirming formation of polydiacetylene in the pore. Investigation of the polarizing characteristics of the observed fluorescence indicated that the
10 polarization direction of fluorescence is confirmed in perpendicular to the rubbing direction, namely along the direction of the oriented pores, thereby confirming orientation control of the polymer chain in the pores and orientation control of the
15 conjugated polymer chains in a macroscopic scale.

Example 5

In this example, a meso-structured tin oxide film having uniaxially oriented tubular pores was prepared by a sol-gel method (dip coating) on the
20 rubbing-treated substrate and by employing a nonionic surfactant having a diacetylene group, and the surfactant was thermally polymerized in the pores to form oriented polymer chains of a conjugated polymer.

The nonionic surfactant B employed in the
25 present example had the following structure:



2.0 g of the nonionic surfactant B were dissolved in 20 g of ethanol, and 5.2 g of tin tetrachloride were added.

5 A silica glass substrate with rubbing-treated polyimide film was prepared in the same manner as in Example 1. The mesostructured tin oxide film was prepared by dip coating with the above solution, and dried in an environment of temperature of 40°C and relative humidity of 20%. At the dip coating, the
10 direction of dip coating was parallel or perpendicular to the rubbing direction of the substrate.

After drying for 10 hours, the film was maintained for 40 hours in an environment of
15 temperature of 40°C and relative humidity of 80%, and the relative humidity was then reduced to 20%. The obtained film was completely transparent.

X-ray diffraction analysis of this film confirmed a strong diffraction peak assigned to the
20 (100) plane of hexagonal porous structures corresponding to a plane interval of 4.60 nm, thereby confirming that the film had a pore structure in which tubular pores are hexagonally packed.

For quantitative evaluation of uniaxial
25 orientation of the tubular pores in this mesostructured tin oxide film, this film was analyzed by in-plane X-ray diffraction. As a result, it was

indicated that the pores in the prepared film were oriented parallel to the rubbing direction, and the distribution of the orientation direction was about 15° from the full width of the half maximum of the diffraction peak in the in-plane rocking curve.

No difference was observed in orientation state between the films of which dip coating direction was parallel or perpendicular to the rubbing direction of the polyimide film, showing that the observed orientation of the tubular pores was restricted by the anisotropy of the substrate.

The above meso-structured tin oxide film was heated for 3 hours at 170°C in nitrogen gas atmosphere to polymerize the diacetylene group of the surfactant. It was indicated by X-ray diffraction analysis that the pore structure shrank in a period thereof but retained the structure by heating. Infrared absorption spectroscopy of the meso-structured film were taken by an ATR method before and after heating. As a result, a strong absorption band of an acetylene bond at 2,260 cm^{-1} observed before heating vanished after the heating, while other peaks did not show change. This result confirmed that the polymerization of the surfactant molecules took place without decomposition of the surfactant molecules. Also fluorescence, not observed in the film before heating, was observed in.

the film after the heating, thus confirming formation of polydiacetylene in the pores. Investigation of the polarizing characteristics of the observed fluorescence indicated that the polarization direction of fluorescence is confirmed in parallel to the rubbing direction, namely along the direction of the oriented pores, thereby confirming orientation control of the polymer chain in the pores and orientation control of the conjugated polymer chains in a macroscopic scale.

Example 6

In this example, a meso-structured titanium oxide film having uniaxially oriented tubular pores was prepared by a sol-gel (dip coating) method on the rubbing-treated substrate by employing a nonionic surfactant having a diacetylene group, and the surfactant was thermally polymerized in the pores to form oriented polymer chains of a conjugated polymer.

The same nonionic surfactant B was employed in the present example as in Example 5.

2.0 g of the nonionic surfactant B were dissolved in 20 g of ethanol, and 3.8 g of titanium tetrachloride were added.

A silica glass substrate with rubbing-treated polyimide film was prepared in the same manner as in Example 1. The mesostructured titanium oxide film was prepared by dip coating with the above solution,

and dried in an environment of temperature of 40°C and relative humidity of 20%. At the dip coating, the direction of dip coating was parallel or perpendicular to the rubbing direction of the substrate.

After drying for 10 hours, the film was maintained for 1 hour in an environment of temperature of 40°C and relative humidity of 80%, and the relative humidity was then reduced to 20%. The obtained film was completely transparent.

X-ray diffraction analysis of this film confirmed a strong diffraction peak assigned to the (100) plane of hexagonal porous structures corresponding to a plane interval of 4.56 nm, thereby confirming that the film had a pore structure in which tubular pores are hexagonally packed.

For quantitative evaluation of uniaxial orientation of the tubular pores in this meso-structured titanium oxide film, this film was analyzed by in-plane X-ray diffraction. As a result, it was indicated that the pores in the prepared film were oriented parallel to the rubbing direction, and the distribution of the orientation direction was about 16° from the full width of the half maximum of the diffraction peak in the in-plane rocking curve.

No difference was observed in orientation state between the films of which dip coating direction was

parallel or perpendicular to the rubbing direction of the polyimide film, showing that the observed orientation of the tubular pores was restricted by the anisotropy of the substrate.

5 The above meso-structured titanium oxide film was heated for 3 hours at 170°C in nitrogen gas atmosphere to polymerize the diacetylene group of the surfactant. The X-ray diffraction analysis showed that although the period of the pore structures
10 shrank by heating but the pore structure was maintained. Infrared absorption spectroscopy of the meso-structured film were taken by an ATR method before and after heating. As a result, a strong
15 absorption band of an acetylene bond at $2,260\text{ cm}^{-1}$ observed before heating vanished after the heating, while other peaks did not show change. This result confirmed that the polymerization of the surfactant molecules took place without decomposition of the surfactant molecules. Also fluorescence, not
20 observed in the film before heating, was observed in the film after the heating, thus confirming formation of polydiacetylene in the pores. Investigation of the polarizing characteristics of the observed fluorescence indicated that the polarization
25 direction of fluorescence is confirmed in parallel to the rubbing direction, namely along the direction of the oriented pores, thereby confirming orientation

control of the polymer chain in the pores and orientation control of the conjugated polymer chains in a macroscopic scale.

Example 7

5 In this example, a meso-structured silica film having uniaxially oriented tubular pores was prepared by a sol-gel (dip coating) method on the rubbing-treated substrate as in Example 1 and the surfactant A employed in Examples 1 to 4, and the surfactant was
10 thermally polymerized in the pores to form oriented polymer chains of a conjugated polymer.

 1.6 g of the cationic surfactant A were dissolved in 20 g of ethanol, and 4.2 g of
tetraethoxysilane were added. This solution was
15 added with 0.27 g of water and 0.8 g of 0.1 M hydrochloric acid and stirred for 2 hours.

 On the rubbing-treated substrate, this solution was applied by dip coating, and dried in an environment of temperature of 25°C and relative
20 humidity of 50%. The dip coating direction was parallel or perpendicular to the rubbing direction of the substrate. The obtained film was completely transparent.

 X-ray diffraction analysis of this film
25 confirmed a strong diffraction peak assigned to the (100) plane of hexagonal porous structures corresponding to a plane interval of 4.08 nm, thereby

confirming that the film had a pore structure in which tubular pores are hexagonally packed.

For quantitative evaluation of uniaxial orientation of the tubular pores in this meso-structured silica film, this film was analyzed by in-
5 plane X-ray diffraction. As a result, it was indicated that the pores in the prepared film were oriented perpendicular to the rubbing direction, and the distribution of the orientation direction was
10 about 8° from the full width of the half maximum of the diffraction peak in the in-plane rocking curve.

No difference was observed in orientation state between the films of which dip coating direction was parallel or perpendicular to the rubbing direction of
15 the polyimide film, showing that the observed orientation of the tubular pores was restricted by the anisotropy of the substrate.

Based on the foregoing, it was shown that a meso-structured silica film having tubular pores of
20 uniaxial orientation was formed on the rubbing treated substrate, utilizing surfactants containing a polymerizable diacetylene group as a hydrophobic group.

The above meso-structured film was heated for 3
25 hours at 170°C in nitrogen gas atmosphere to polymerize the diacetylene group of the surfactant. Infrared absorption spectroscopy of the meso-

structured film were taken by an ATR method before and after heating. As a result, a strong absorption band of acetylene bond at $2,260\text{ cm}^{-1}$ observed before heating vanished after the heating, while other peaks did not show change. This result confirmed that the polymerization of the surfactant molecules took place without decomposition of the surfactant molecules. Also fluorescence, not observed in the film before heating, was observed in the film after the heating, thus confirming formation of polydiacetylene in the pores. Investigation of the polarizing characteristics of the observed fluorescence indicated that the polarization direction of fluorescence is confirmed in perpendicular to the rubbing direction, namely along the direction of the oriented pores, thereby confirming orientation control of the polymer chain in the pores and orientation control of the conjugated polymer chains in a macroscopic scale.

Example 8

In this example, a meso-structured silica film having uniaxially oriented tubular pores was prepared by a sol-gel (dip coating) method on the rubbing-treated substrate as in Example 1 and a cationic surfactant containing a thiophene group, and the surfactant was subjected to a chemical oxidation polymerization in the pores to form oriented polymer

chains of a conjugated polymer.

A cationic surfactant E employed in the present example had a structure shown in Fig. 5E.

2.3 g of the cationic surfactant E were
5 dissolved in 20 g of ethanol, and 4.2 g of tetraethoxysilane were added. This solution was added with 0.27 g of water and 0.8 g of 0.1 M hydrochloric acid and stirred for 2 hours to obtain a precursor solution.

10 On the rubbing-treated substrate, this solution was applied by dip coating, and dried in an environment of temperature of 25°C and relative humidity of 50%. At the dip coating, the direction of dip coating was parallel or perpendicular to the
15 rubbing direction of the substrate. The obtained film was completely transparent.

X-ray diffraction analysis of this film confirmed a strong diffraction peak assigned to the (100) plane of hexagonal porous structures
20 corresponding to a plane interval of 4.12 nm, thereby confirming that the film had a pore structure in which tubular pores are hexagonally packed.

For quantitative evaluation of uniaxial orientation of the tubular pores in this meso-
25 structured silica film, this film was analyzed by in-plane X-ray diffraction. As a result, it was indicated that the pores in the prepared film were

oriented perpendicular to the rubbing direction.

No difference was observed in orientation state between the films of which dip coating direction was parallel or perpendicular to the rubbing direction of the polyimide film, showing that the observed
5 orientation of the tubular pores was restricted by the anisotropy of the substrate.

Based on the foregoing, it was shown that a meso-structured silica film having tubular pores of
10 uniaxial orientation was formed on the rubbing-treated substrate, utilizing surfactants containing a polymerizable thiophene group as a hydrophobic group.

The above meso-structured film was immersed in diethylether solution of iron chloride for 1 minute
15 at the room temperature, to polymerize the thiophene group of the surfactant. In ultraviolet-visible absorption spectra of the meso-structured film before and after the immersion, a broad absorption at 500 nm was observed only in the spectrum after the immersion,
20 thereby confirming the polymerization reaction of the surfactant molecules. Formation of polythiophene in the pores was thus confirmed. The polarized absorption of the mesostructured silica film showed the anisotropy. This fact confirmed orientation
25 control of the polymer chain in the pores and orientation control of the conjugated polymer chains in a macroscopic scale.

Example 9

In this example, a meso-structured silica film having uniaxially oriented tubular pores was prepared by a sol-gel (spin coating) method on the rubbing-
5 treated substrate as in Example 1 and a cationic surfactant containing a pyrrole group, and the surfactant was subjected to a chemical oxidation polymerization in the pores to form oriented polymer chains of a conjugated polymer.

10 A cationic surfactant D employed in the present example had a structure shown in Fig. 5D.

1.6 g of the cationic surfactant D were dissolved in 20 g of ethanol, and 4.2 g of
tetraethoxysilane were added. This solution was added
15 with 0.27 g of water and 0.8 g of 0.1 M hydrochloric acid and stirred for 2 hours to obtain a precursor solution.

On the rubbing-treated substrate, this solution was applied by spin coating. The spin
20 coating was conducted with a revolution of 2,000 rpm and a rotation time of 20 seconds. The prepared film was dried in an environment of temperature of 25°C and relative humidity of 50%. The obtained film was completely transparent.

25 X-ray diffraction analysis of this film confirmed a strong diffraction peak assigned to the (100) plane of hexagonal porous structures

corresponding to a plane interval of 4.10 nm, thereby confirming that the film had a pore structure in which tubular pores are hexagonally packed.

For quantitative evaluation of uniaxial
5 orientation of the tubular pores in this meso-structured silica film, this film was analyzed by in-plane X-ray diffraction. As a result, it was indicated that the pores in the prepared film were oriented parallel to the rubbing direction, and the
10 distribution of the orientation direction was about 13° from the full width of the half maximum of the diffraction peak in the in-plane rocking curve.

Based on the foregoing, it was shown that a
meso-structured silica film having tubular pores of
15 uniaxial orientation was formed on the rubbing-treated substrate, utilizing surfactants containing a polymerizable pyrrole group as a hydrophobic group.

The above meso-structured film was immersed in a solution of iron chloride in diethylether for 1
20 minute at the room temperature, to polymerize the pyrrole group of the surfactant. In an ultraviolet-visible-near infrared absorption spectra of the meso-structured film before and after the immersion, a broad absorption at 1,000 nm was observed only in the
25 spectrum after the immersion, thereby confirming the polymerization reaction of the surfactant molecules. Formation of polypyrrole in the pores was thus

confirmed. Investigation of the polarizing characteristics of the observed absorption indicated that the polarization direction of absorption is confirmed in parallel to the rubbing direction, namely along the direction of the oriented pores, thereby confirming orientation control of the polymer chain in the pores and orientation control of the conjugated polymer chains in a macroscopic scale.

Example 10

10 In this example, a meso-structured silica film having uniaxially oriented tubular pores was prepared by a sol-gel (mist coating) method on the rubbing-treated substrate as in Example 1 and a cationic surfactant containing a pyrrole group, and the
15 surfactant was subjected to a chemical oxidation polymerization in the pores to form oriented polymer chains of a conjugated polymer.

The cationic surfactant D employed in the present example had a structure shown in Fig. 5D.

20 1.6 g of the cationic surfactant D were dissolved in 20 g of ethanol, and 4.2 g of tetraethoxysilane were added. This solution was added with 0.27 g of water and 0.8 g of 0.1 M hydrochloric acid and stirred for 2 hours to obtain a
25 precursor solution.

On the rubbing-treated substrate, the precursor solution was applied by mist coating, and the

prepared film was dried in an environment of temperature of 25°C and relative humidity of 50%. The obtained film was completely transparent.

X-ray diffraction analysis of this film confirmed a strong diffraction peak assigned to the (100) plane of hexagonal porous structures corresponding to a plane interval of 4.12 nm, thereby confirming that the film had a pore structure in which tubular pores are hexagonally packed.

For quantitative evaluation of uniaxial orientation of the tubular pores in this meso-structured silica film, this film was analyzed by in-plane X-ray diffraction. As a result, it was indicated that the pores in the prepared film were oriented parallel to the rubbing direction, and the distribution of the orientation direction was about 14° from the full width of the half maximum of the diffraction peak in the in-plane rocking curve.

Based on the foregoing, it was shown that a meso-structured silica film having tubular pores of uniaxial orientation was formed on the rubbing-treated substrate, utilizing surfactants containing a polymerizable pyrrole group as a hydrophobic group.

The above meso-structured film was immersed in a diethylether solution of iron chloride for 1 minute at the room temperature, to polymerize the pyrrole group of the surfactant. In ultraviolet-visible-near

infrared absorption spectra of the meso-structured film before and after the immersion, a broad absorption at 1,000 nm was observed only in the spectrum after the immersion, thereby confirming the polymerization reaction of the surfactant molecules. Formation of polypyrrole in the pores was thus confirmed. Investigation of the polarizing characteristics of the observed absorption indicated that the polarization direction of absorption is confirmed in parallel to the rubbing direction, namely along the direction of the oriented pores, thereby confirming orientation control of the polymer chain in the pores and orientation control of the conjugated polymer chains in a macroscopic scale.

Example 11

In this example, a meso-structured silica film having uniaxially oriented tubular pores was prepared by a soft lithography method in an arbitrary position on the rubbing-treated substrate as in Example 1 and a surfactant A employed in Examples 1 to 4, and the surfactant was subjected to a thermal polymerization in the pores to form oriented polymer chains of a conjugated polymer.

1.6 g of the cationic surfactant A were dissolved in 20 g of ethanol, and 4.2 g of tetraethoxysilane were added. This solution was added with 0.27 g of water and 0.8 g of 0.1 M

hydrochloric acid and stirred for 2 hours to obtain a precursor solution.

On the rubbing-treated substrate, the micromold made of polydimethylsiloxane was pressed and the precursor solution was poured from the end of the mold, whereby the solution was introduced by capillary action into the mold. After standing for 5 hours, the mold was removed from the substrate to obtain the patterned meso-structured film.

After drying in the air, the substrate was confirmed that a transparent film was formed only in an area of coating by the soft lithography method.

X-ray diffraction analysis of this film confirmed a strong diffraction peak assigned to the (100) plane of hexagonal porous structures corresponding to a plane interval of 4.07 nm, thereby confirming that the film had a pore structure in which tubular pores are hexagonally packed.

For quantitative evaluation of uniaxial orientation of the tubular pores in this meso-structured silica film, this film was analyzed by in-plane X-ray diffraction. As a result, it was indicated that the pores in the prepared film were oriented perpendicular to the rubbing direction, and the distribution of the orientation direction was about 11° from the full width of the half maximum of the diffraction peak in the in-plane rocking curve.

Based on the foregoing, it was shown that a patterned meso-structured silica film having tubular pores of uniaxial orientation was formed on the rubbing-treated substrate, utilizing surfactants
5 containing a polymerizable diacetylene group as a hydrophobic group.

The above meso-structured film was heated for 3 hours at 170°C in nitrogen gas atmosphere to polymerize the diacetylene group of the surfactant.
10 Infrared absorption spectroscopy of the meso-structured film were taken by an ATR method before and after heating. As a result, a strong absorption band of acetylene bond at $2,260\text{ cm}^{-1}$ observed before heating vanished after the heating, while other peaks
15 did not show change. This result confirmed that the polymerization of the surfactant molecules took place without decomposition of the surfactant molecules. Also fluorescence, not observed in the film before heating, was observed in the film after the heating,
20 thus confirming formation of polydiacetylene in the pore. Investigation of the polarizing characteristics of the observed fluorescence indicated that the polarization direction of fluorescence is confirmed in perpendicular to the
25 rubbing direction, namely along the direction of the oriented pores, thereby confirming orientation control of the polymer chain in the pores and

orientation control of the conjugated polymer chains in a macroscopic scale.

Example 12

In this example, a meso-structured silica film
5 having uniaxially oriented tubular pores was prepared by a pen lithography method in an arbitrary position on the rubbing-treated substrate as in Example 1 and a surfactant A employed in Examples 1 to 4, was subjected to a thermal polymerization in the pores to
10 form oriented polymer chains of a conjugated polymer.

1.6 g of the cationic surfactant A were dissolved in 20 g of ethanol, and 4.2 g of tetraethoxysilane were added. This solution was added with 0.27 g of water and 0.8 g of 0.1 M
15 hydrochloric acid and stirred for 2 hours to obtain a precursor solution.

On the rubbing-treated substrate, the solution was patterned by a pen lithography method, and the prepared film was dried in the air at the room
20 temperature. The pen lithography was conducted under conditions of a pen orifice of 50.0 μm , a stage speed of 2.5 cm/s and a fluid supply rate of 4.0 cm.

In an observation of the substrate after drying in the air, it was confirmed that a transparent film
25 was formed only in an area of coating by the pen lithography method.

X-ray diffraction analysis of this film

confirmed a strong diffraction peak assigned to the (100) plane of hexagonal porous structures corresponding to a plane interval of 4.09 nm, thereby confirming that the film had a pore structure in which tubular pores are hexagonally packed.

For quantitative evaluation of uniaxial orientation of the tubular pores in this meso-structured silica film, this film was analyzed by in-plane X-ray diffraction. As a result, it was indicated that the pores in the prepared film were oriented perpendicular to the rubbing direction, and the distribution of the orientation direction was about 10° from the full width of the half maximum of the diffraction peak in the in-plane rocking curve.

Based on the foregoing, it was shown that a patterned meso-structured silica film having tubular pores of uniaxial orientation was formed on the rubbing-treated substrate, utilizing surfactants containing a polymerizable diacetylene group as a hydrophobic group.

The above meso-structured film was heated for 3 hours at 170°C in nitrogen gas atmosphere to polymerize the diacetylene group of the surfactant. Infrared absorption spectroscopy of the meso-structured film were taken by an ATR method before and after heating. As a result, a strong absorption band of acetylene bond at 2,260 cm⁻¹ observed before

heating vanished after the heating, while other peaks did not show change. This result confirmed that the polymerization of the surfactant molecules took place without decomposition of the surfactant molecules.

- 5 Also fluorescence, not observed in the film before heating, was observed in the film after the heating, thus confirming formation of polydiacetylene in the pores. Investigation of the polarizing characteristics of the observed fluorescence
- 10 indicated that the polarization direction of fluorescence is confirmed in perpendicular to the rubbing direction, namely along the direction of the oriented pores, thereby confirming orientation control of the polymer chain in the pores and
- 15 orientation control of the conjugated polymer chains in a macroscopic scale.

Example 13

- In this example, a meso-structured silica film having uniaxially oriented tubular pores was prepared
- 20 by an ink jet method in an arbitrary position on the rubbing-treated substrate as in Example 1 and a surfactant A employed in Examples 1 to 4, was subjected to a thermal polymerization in the pores to form oriented polymer chains of a conjugated polymer.

- 25 1.6 g of the cationic surfactant A were dissolved in 20 g of ethanol, and 4.2 g of tetraethoxysilane were added. This solution was

added with 0.27 g of water and 0.8 g of 0.1 M hydrochloric acid and stirred for 2 hours to obtain a precursor solution.

On the rubbing-treated substrate, the solution
5 was applied by an ink jet method in a pattern, and the prepared film was dried in the air at the room temperature.

In an observation of the substrate after drying
in the air, it was confirmed that a transparent film
10 was formed only in an area formed by the ink jet method.

X-ray diffraction analysis of this film confirmed a strong diffraction peak assigned to the (100) plane of hexagonal porous structures
15 corresponding to a plane interval of 4.12 nm, thereby confirming that the film had a pore structure in which tubular pores are hexagonally packed.

For quantitative evaluation of uniaxial orientation of the tubular pores in this meso-
20 structured silica film, this film was analyzed by in-plane X-ray diffraction. As a result, it was indicated that the pores in the prepared film were oriented perpendicular to the rubbing direction, and the distribution of the orientation direction was
25 about 12° from the full width of the half maximum of the diffraction peak in the in-plane rocking curve.

Based on the foregoing, it was shown that a

meso-structured silica film having tubular pores of uniaxial orientation was formed on the rubbing-treated substrate, utilizing surfactants containing a polymerizable diacetylene group as a hydrophobic group.

The above meso-structured film was heated for 3 hours at 170°C in nitrogen gas atmosphere to polymerize the diacetylene group of the surfactant. Infrared absorption spectroscopy of the meso-structured film were taken by an ATR method before and after heating. As a result, a strong absorption band of acetylene bond at 2,260 cm^{-1} observed before heating vanished after the heating, while other peaks did not show change. This result confirmed that the polymerization of the surfactant molecules took place without decomposition of the surfactant molecules. Also fluorescence, not observed in the film before heating, was observed in the film after the heating, thus confirming formation of polydiacetylene in the pores. Investigation of the polarizing characteristics of the observed fluorescence indicated that the polarization direction of fluorescence is confirmed in perpendicular to the rubbing direction, namely along the direction of the oriented pores, thereby confirming orientation control of the polymer chain in the pores and orientation control of the conjugated polymer chains

in a macroscopic scale.

Comparative Example

An ethanol solution of tin tetrachloride and the nonionic surfactant B, was prepared in the same manner as in Example 5, and this precursor solution was applied by dip coating on an isotropic silica glass substrate without coating or particular processing on the surface.

The coated substrate was dried, as in Example 5, for 10 hours in an environment of temperature of 40°C and relative humidity of 20%, then maintained for 40 hours in an environment of temperature of 40°C and relative humidity of 80%, and the relative humidity was then reduced to 20%. The obtained film was completely transparent.

X-ray diffraction analysis of this film confirmed a strong diffraction peak assigned to the (100) plane of hexagonal porous structures corresponding to a plane interval of 4.60 nm, thereby confirming that the film had a pore structure in which tubular pores are hexagonally packed.

For quantitative evaluation of uniaxial orientation of the tubular pores in this meso-structured tin oxide film, this film was analyzed by in-plane X-ray diffraction. As a result, the orientation state of the pores in the prepared film was completely isotropic and no increase in the X-ray

diffraction intensity in a particular direction was observed.

The above meso-structured tin oxide film was heated for 3 hours at 170°C in nitrogen gas atmosphere to polymerize the diacetylene group of the surfactant. It was indicated by X-ray diffraction analysis that the pore structures shrank in a period thereof but retained the pore structure by heating. Infrared absorption spectroscopy of the meso-structured film were taken by an ATR method before and after heating. As a result, a strong absorption band of an acetylene bond at $2,260\text{ cm}^{-1}$ observed before heating vanished after the heating, while other peaks did not show change. This result confirmed that the polymerization of the surfactant molecules took place without decomposition of the surfactant molecules. Also fluorescence, not observed in the film before heating, was observed in the film after the heating, thus confirming formation of polydiacetylene in the pores. In an investigation of the polarizing characteristics of the observed fluorescence, dependence on polarization was not observed in the intensity of the fluorescence, thus confirming that any specific orientation was absent in the polymer chains.

As described above, according to the present invention, the meso-structured film having tubular

pores of uniaxial orientation can be formed on the substrate with surface anisotropy, utilizing polymerizable surfactants. Further, polymerization of the surfactant in the uniaxially oriented pores, a
5 structure in which conjugated polymers are oriented in one direction can be obtained.

CLAIMS

1. A structured material having a layer with uniaxial oriented tubular pores provided on a substrate;

5 wherein said tubular pores are parallel to an interface of said substrate and said layer, and contain a conductive polymer material having a function of a surfactant therein.

2. The structured material according to claim 1,
10 wherein said polymer material is selected from the group consisting of a polydiacetylene derivative, a polythiophene derivative and a polypyrrole derivative.

3. The structured material according to claim 1,
 wherein said layer contains a material selected from
15 the group consisting of silicon oxide, tin oxide and titanium oxide.

4. The structured material according to claim 1, wherein said layer contains an organic substance.

5. The structured material according to claim 1,
20 wherein a surface of the substrate in contact with said layer has anisotropy.

6. A method for producing a structured material comprising steps of:

 providing a substrate showing the anisotropy on
25 a surface;

 applying a solution including a surfactant which has a functional group for polymerization in a

molecular structure, a solvent therefor, and a solute different from said surfactant to said substrate; and

allowing said substrate to stand for a predetermined time for causing said surfactant to
5 assemble in a predetermined direction based on the anisotropy of the substrate.

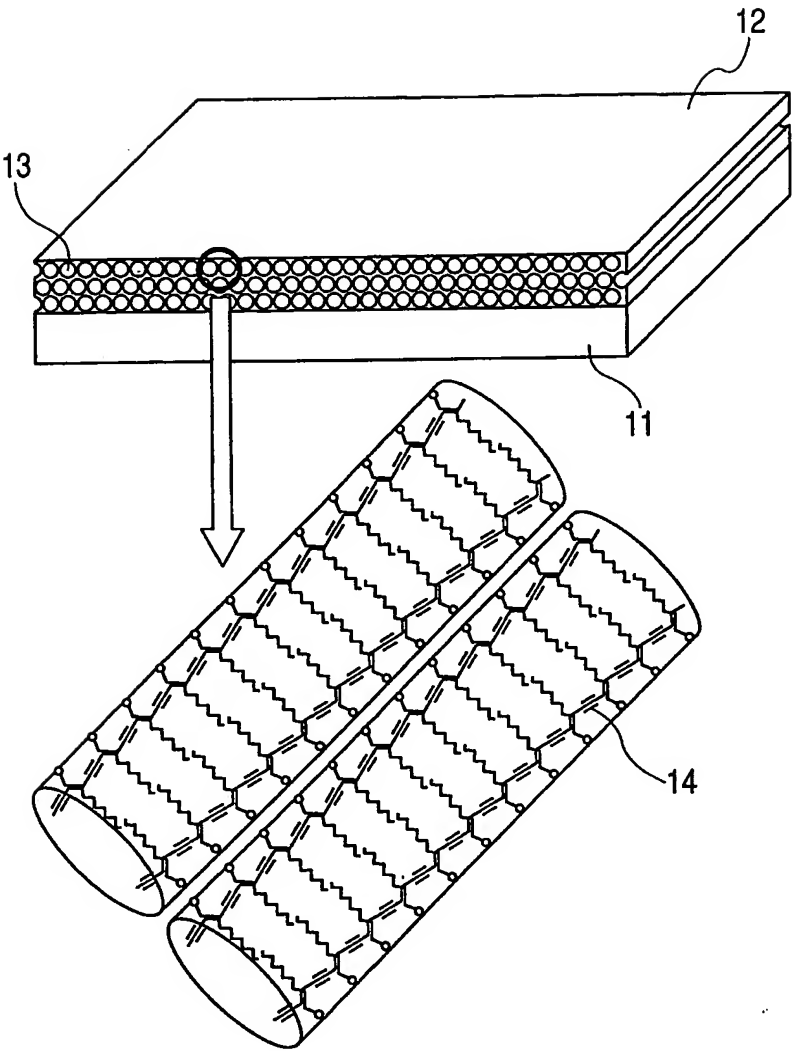
7. The method according to claim 6, wherein said surfactant has diacetylene, thiophene or pyrrole group in the molecular structure.

10 8. The method according to claim 6, wherein, in said standing step, the substrate is exposed to water vapor.

9. The method according to claim 6, further comprising a step of polymerizing the surfactant
15 after the standing step.

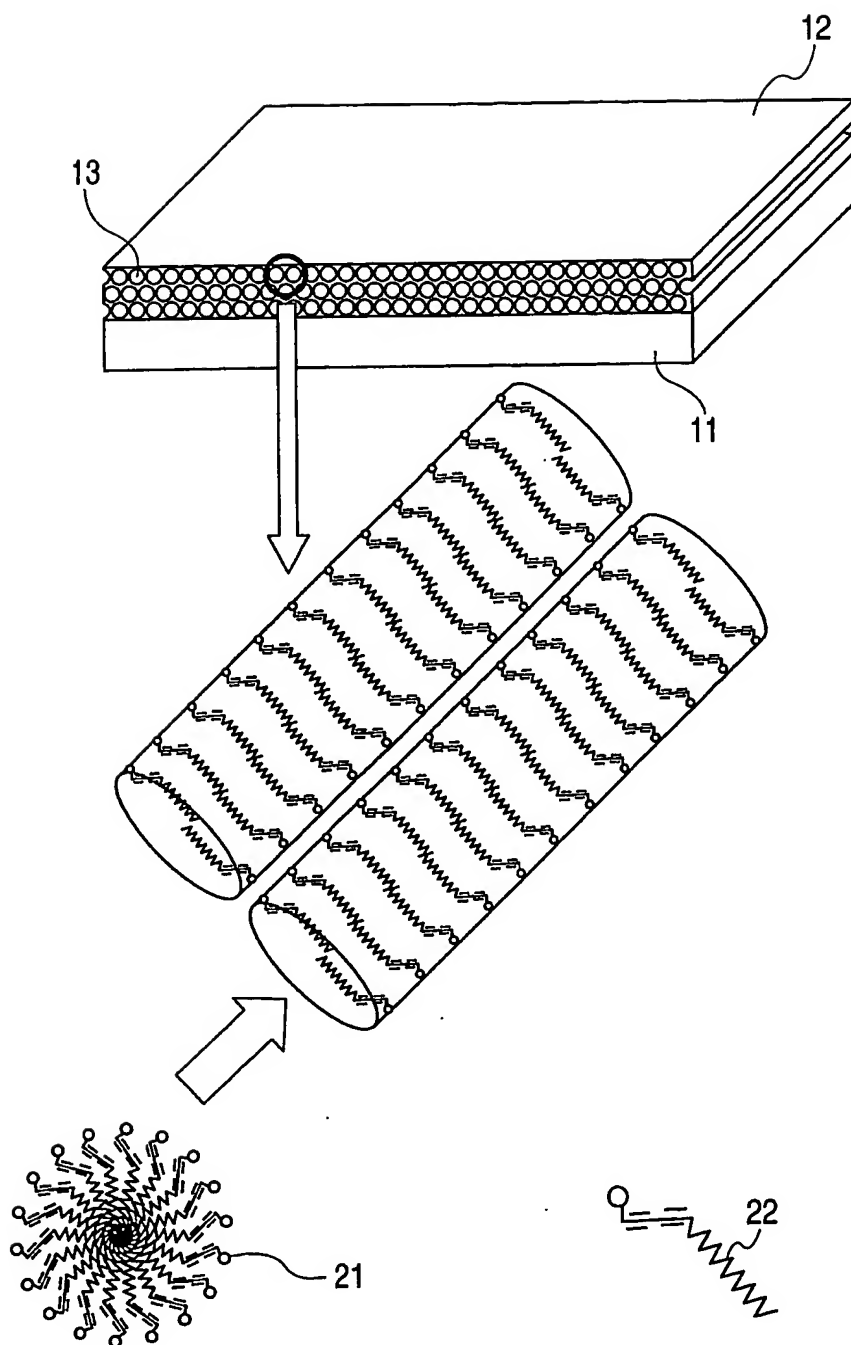
10. The method according to claim 6, wherein said polymerizing step is executed by thermal polymerization, photopolymerization, or chemical polymerization.

FIG. 1



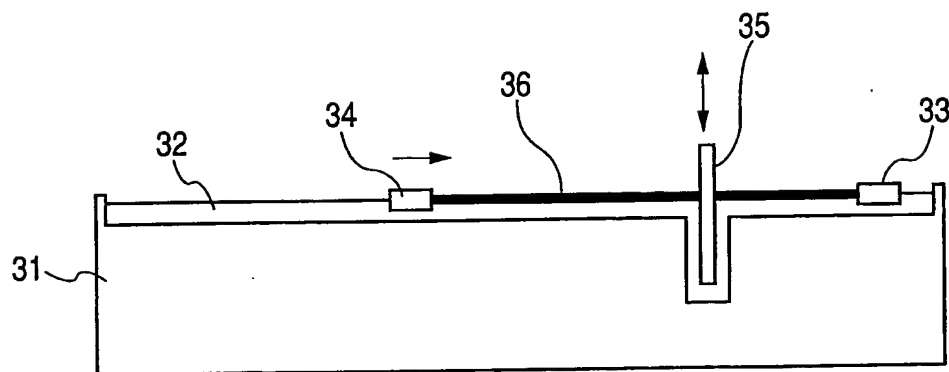
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FIG. 2



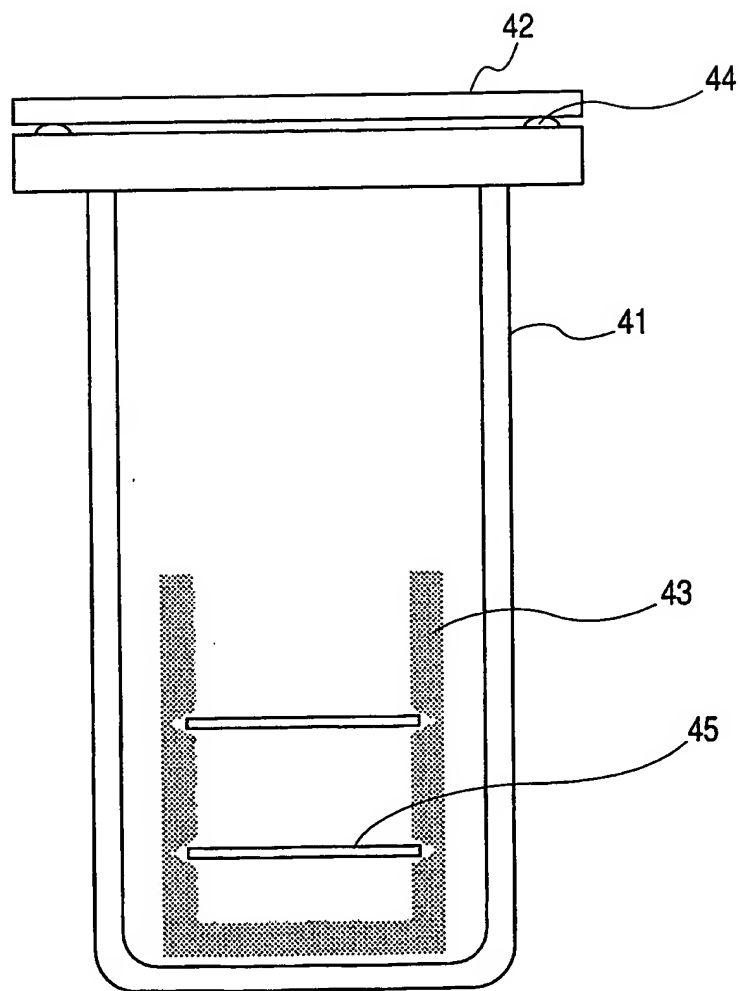
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FIG. 3

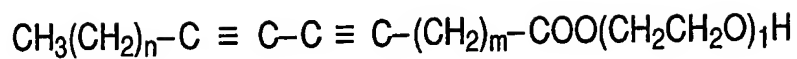
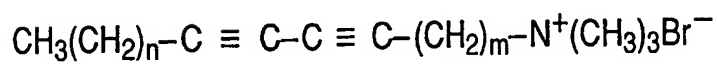
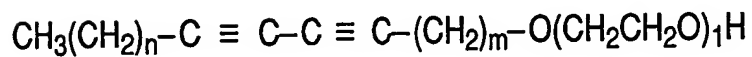
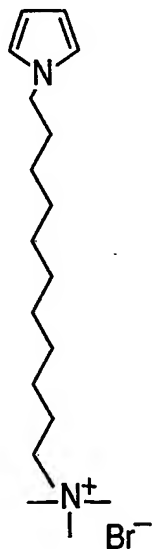
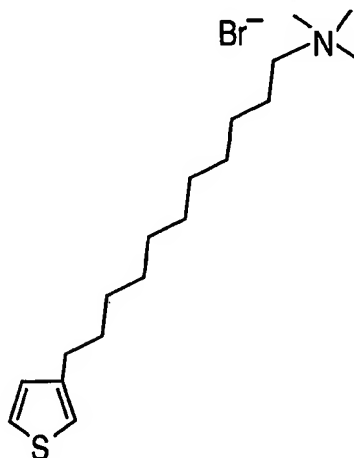


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FIG. 4

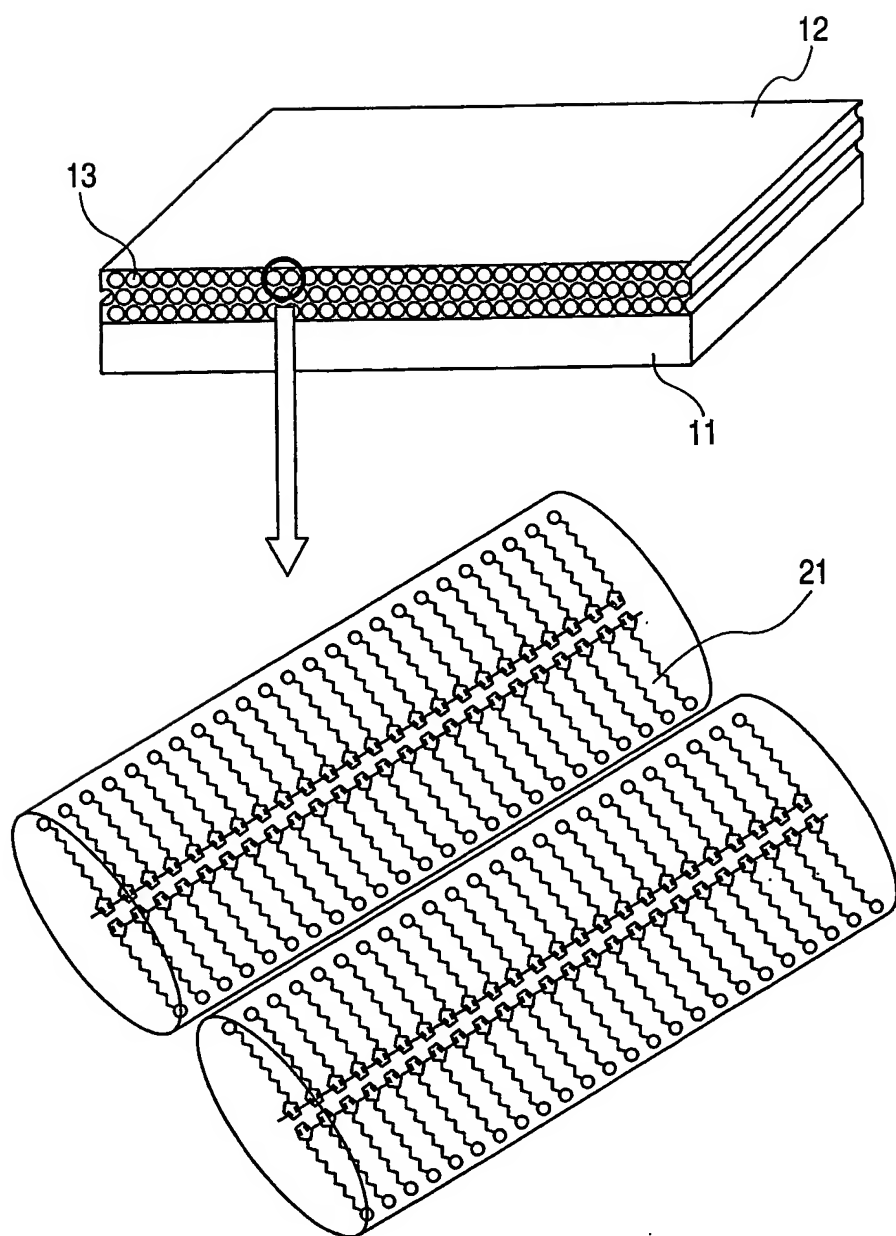


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FIG. 5A*FIG. 5B**FIG. 5C**FIG. 5D**FIG. 5E*

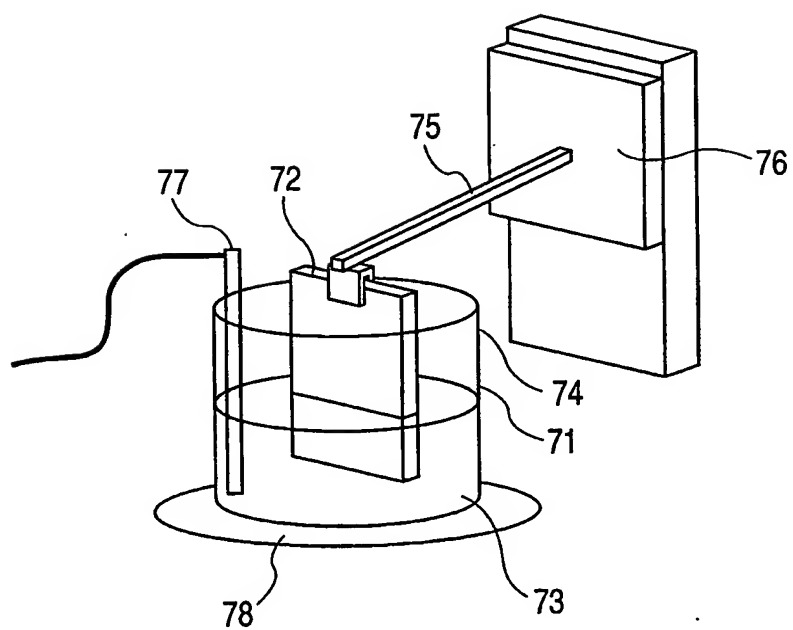
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FIG. 6



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FIG. 7



INTERNATIONAL SEARCH REPORT

International Application No
PCT/JP2004/010888

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 H01B1/12 B82B3/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 H01B B82B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, INSPEC, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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A	ANGEWANDTE CHEMIE, INTERNATIONAL EDITION, vol. 40, no. 20, 2001, pages 3803-3806, XP002304962 WEINHEIM cited in the application page 3803, right-hand column, paragraph 2 - page 3805, left-hand column, paragraph 1 Scheme 1	1-10
A	PATENT ABSTRACTS OF JAPAN vol. 2000, no. 22, 9 March 2001 (2001-03-09) -& JP 2001 145831 A (CANON INC), 29 May 2001 (2001-05-29) abstract; figures -/--	1-10

☒ Further documents are listed in the continuation of box C.

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Date of the actual completion of the international search

10 November 2004

Date of mailing of the international search report

01/12/2004

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INTERNATIONAL SEARCH REPORT

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A	US 2002/046682 A1 (BRINKER CHARLES JEFFREY ET AL) 25 April 2002 (2002-04-25) paragraph '0097!; claim 21; figures 1,5	

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Information on patent family members

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Application No

PCT/JP2004/010888

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